

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 603 697 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
03.09.1997 Bulletin 1997/36

(51) Int. Cl.⁶: **C04B 41/46**, C07F 9/09,
C08G 65/32

(21) Application number: 93120051.3

(22) Date of filing: 13.12.1993

(54) Process for imparting oil- and water-repellency to the surface of porous ceramic materials

Verfahren um die Oberfläche von porösen, keramischen Materialien öl und wasserabweisende
Eigenschaften zu Verleihen

Méthode pour rendre la surface de matériaux céramiques poreux résistante à l'huile et à l'eau

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT
SE

(30) Priority: 16.12.1992 IT MI922860

(43) Date of publication of application:
29.06.1994 Bulletin 1994/26

(73) Proprietor: **AUSIMONT S.p.A.**
I-20121 Milano (IT)

(72) Inventors:
• Strepparola, Ezio
I-24047 Treviglio (BG) (IT)
• Boselli, Viviana
I-20129 Milano (IT)
• Scapin, Mauro
I-21052 Busto Arsizio (VA) (IT)

(74) Representative: **Simeoni, Lucio, Dr. et al**
Sama Patents,
Via Morgagni, 2
20129 Milano (IT)

(56) References cited:
DE-A- 2 413 970 **US-A- 3 188 340**
US-A- 3 492 374

• **DATABASE WPI Section Ch, Week 9312, Derwent**
Publications Ltd., London, GB; Class D21, AN
93-096729 & JP-A-5 039 209 (KAO CORP.) 19
February 1993

• **DATABASE WPI Section Ch, Week 9240, Derwent**
Publications Ltd., London, GB; Class D21, AN
92-3228086 & JP-A-4 235 908 (KAO CORP.) 25
August 1992

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 603 697 B1

Description

The present invention relates to a process for imparting oil- and water-repellency to the surfaces of porous ceramic materials and in particular of "cotto".

In the building industry, a broad use is made of porous ceramic materials, which exhibit a dull and rather irregular surface, because after baking they were not subjected to vitrification and/or enamelling treatments. A typical example is the so-called "Tuscan cotto", which is generally utilized as flooring material. It is a ceramic obtained by baking in an oven a mixing of clayish materials mainly composed of ores based on alumino-silicates, such as illite, illite-smectite, kaolinite, clorite, etc.

The porosity and the colour, which are typical of this type of ceramics, are highly appreciated for aesthetical reasons, but they involve considerable difficulties as regards cleaning. In fact dirtiness, which can be carried by water or by oily substances, is easily absorbed and retained in the material pores, thereby causing a color alteration, and it is difficult to be removed by means of conventional washing techniques. The application of hydrocarbon-based waxes gives quite unsatisfactory results, as such products, although imparting an excellent water-repellency, exhibit a great affinity for oily products, wherefore, instead of repelling the fatty substances, favour the absorption of same.

It is known to use polyperfluoroalkylene oxides having perfluoroalkyl end groups for the protection of marble, stones, tiles, concrete and similar materials from the action of polluting atmospheric agents (see for example U.S. patent 4,499,146). Such products, besides imparting water- and oil-repellency properties, are endowed with a high permeability to gases and vapors, wherefore they permit to the protected material to "breathe". Furthermore, thanks to a very low refraction index, the polyperfluoroalkylene oxides do not alter the aspect and original color of the material, since optical interference and/or reflection phenomena do not occur.

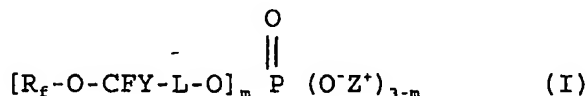
The presence of porosity in the material to be protected leads to migration phenomena of the polyperfluoroalkylene oxides from the surface to the interior of the material, with consequent decrease of the protective action in the course of time. A considerable improvement with respect to U.S. patent 4,499,146 is represented therefore by the use of perfluoroalkylene oxides functionalized with groups, which are capable of fixing the product to the substrate to be protected, such as carboxylic, estereal, amidic, hydroxylic, isocyanic, epoxy, silanic etc. groups, as is described in U.S. patents 4,745,009 and 4,746,550. Many other functionalized polyperfluoroalkylene oxides are described in U.S. patent 4,085,137.

On the basis of the tests carried out by the Applicant, most of the products described in the above-cited patents are not suited to solve the technical problem underlying the present invention, i.e. to provide products which are capable of:

- (a) imparting a higher water- and oil-repellency to the surface of porous ceramic materials, and in particular to the surface of "cotto";
- (b) remaining anchored to the surface of the treated material for a long time, in order not to cause migration to the interior of the same material and to withstand repeated washings with usual cleaners;
- (c) not modifying the aesthetical characteristics of the treated material, in particular the color;
- (d) being permeable to gases and vapors, in particular to water vapor;
- (e) being applicable with economic methods, easy to be carried into practice.

The Applicant has now surprisingly found that the phosphoric monoesters derived from polyperfluoroalkylene oxides fully meet the above-listed requirements.

Thus, it is an object of the present invention to provide a process for imparting oil- and water-repellency to the surface of a porous ceramic material, which process comprises applying onto said surface, a phosphoric monoester having the formula:



where:

L is a divalent organic group; $m = 1$; Y is -F or -CF₃; Z⁺ is selected from: H⁺; M⁺ where M is an alkalimetal; N(R)₄⁺ where groups R, like or different from each other, are H or C₁-C₆ alkyls; R_f is a polperfluoroalkylene oxide chain.

A further object of the present invention are the phosphoric monoesters having formula (I) and the process for pre-

paring them.

According to the process of the present invention, the phosphoric monomester of formula (I) can be optionally mixed with a phosphoric diester, corresponding to formula (I) where $m = 2$, and/or a phosphoric triester, corresponding to formula (I), where $m = 3$, in such amounts that the monoester content is at least equal to 80 mols-%.

5 By L is meant a divalent organic group, preferably non-fluorinated, which can be selected from:

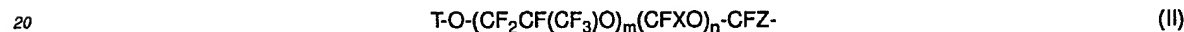
- (a) $-\text{CH}_2-(\text{OCH}_2\text{CH}_2)_n-$, where n is an integer from 0 to 3;
(b) $-\text{CO}-\text{NR}'-(\text{CH}_2)_q-$, where R' is H or a C_1 - C_4 alkyl; q is an integer from 1 to 4.

10 Groups R_i have preferably a number average molecular weight Mn ranging from 250 to 3,000, preferably from 400 to 1,000, and are composed of one or more repeating units randomly distributed along the chain and selected from:

(C₃F₆O); (C₂F₄O); (CFXO), where X is -F or -CF₃;
(CYZ-CF₂CF₂O), where Y and Z, like or different from each other, are F, Cl or H.

15 Poly-perfluoroalkylene oxide chains R_f can be selected in particular from the following classes:

- (a)



where:

T is a (per)fluoroalkyl group selected from:

25 -CF₃, -C₂F₅, -C₃F₇, -CF₂Cl, -C₂F₄Cl, -C₃F₆Cl; X is -F or -CF₃; Z is -F, -Cl or -CF₃; m and n are numbers such that the n/m ranges from 0.01 to 0.5 and the molecular weight is in the above-indicated range;

- (b)

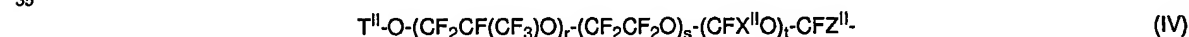


30 where:

T¹ is a (per)fluoroalkyl group selected from:

-CF₃, -C₂F₅, -CF₂Cl, -C₂F₄Cl; Z' is -F or -Cl; p and q are numbers such that the q/p ratio ranges from 0.5 to 2 and the molecular weight is in the above indicated range;

- (c)

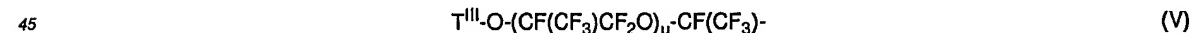


where:

T^{II} is a (per)fluoroalkyl group selected from:

40 -CF₃, -C₂F₅, -C₃F₇, -CF₂Cl, -C₂F₄Cl, -C₃F₆Cl; X^{II} is -F or -CF₃; Z^{II} is -F, -Cl or -CF₃; r, s and t are numbers such that r + s ranges from 1 to 50, the t/(r+s) ratio ranges from 0.01 to 0.05 and the molecular weight is in the above indicated range;

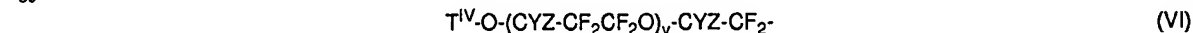
- (d)



where:

T^{III} is -C₂F₅ or -C₃F₇; u is a number such that the molecular weight is in the above indicated range;

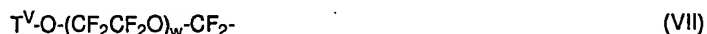
- (e)



where:

Y and Z, like or different from each other, are F, Cl or H; T^{IV} is -CF₃, -C₂F₅ or -C₃F₇; v is a number such that the molecular weight is in the above indicated range;

- (f)



where:

T^V is $-CF_3$ or $-C_2F_5$; w is a number such that the molecular weight is in the above indicated range.

The phosphoric monoester of formula (I) can be utilized either in acid form ($Z = H^+$), or salified with an alkaline metal hydroxide ($Z = M^+$, where $M = Li, Na, K$, etc.), or with ammonia or with an amine ($Z = N(R)_4^+$). Groups R can be optionally substituted by hydroxyls or they can be linked to one another so as to form a ring on the nitrogen atom, for example of the morpholinic type.

The amount of phosphoric monoester of formula (I) to be utilized in order to obtain an effective water- and oil-repellency action varies over a very wide range as a function of the surface characteristics of the material to be treated and of the molecular weight of the monoester itself. For example, for a typical "Tuscan cotto" there are applicable about 0.5 mg/cm² of a product of formula (I) having a R_f chain with $M_n = 700$. As a function of the specific conditions, for those skilled in the art it is sufficient to carry out a few tests for determining the optimum amount to be applied.

The monoester of formula (I) is preferably applied in the form of solution, at concentrations generally ranging from 0.1 to 5% by weight, preferably from 0.5 to 2% by weight.

Suitable solvents, or mixtures of solvents, can be selected from the following classes: aliphatic alcohols having 1 to 4 carbon atoms, fluorocarbons and chlorofluorocarbons, optionally containing hydrogen, ketones and esters having 3 to 10 carbon atoms, methylchloroform, low molecular weight (generally from 400 to 1,000) polyperfluoroalkylene oxide having fluoroalkyl end groups, etc. It is possible to use also solvent/non-solvent mixtures such as, for example, ketone/water mixtures or alcohols/water mixtures in ratios ranging from 10:90 to 90:10 by volume, or also (chloro)fluorocarbons/dimethylformamide mixtures or methylchloroform/dimethylformamide mixtures in ratios ranging from 1:1 to 3:1 by volume.

The choice of the most suitable solvent depends on several factors. First of all, the solvent must be capable of dissolving, in the desired concentration, the specific product of formula (I) which is to be utilized. To this end it is sufficient to carry out some solubility tests.

Furthermore, the solvent must quickly dry, leaving the treated surface free from halos. In order to check whether the selected solvent meets this requirement, the following test can be conducted. 20 ml of solvent are dropped onto a "Tuscan cotto" tile having a surface of 450 cm²; two hours after the application, at room temperature (25°C) the "cotto" surface must be dry and free from halos.

The solvent suitability shall be further checked by applying onto a "Tuscan cotto" test piece, a solution composed of the solvent to be tested and of the product of formula (I) to be utilized, at the desired concentration. The surface so treated is subjected to a water-repellency test according to the method described later on herein. The solvent is to be considered as suitable if a sphericity index ranging from A to C is obtained (see the scale reported later on herein) and no dark halo appears at the base of the water drop (which halo indicates the absorption begin) in the ten minutes following the deposition of the drop. This additional test in order to check the solvent suitability is particularly important when it is desired to utilize solvent/non-solvent mixtures. In these cases, in fact, the solvent could evaporate too soon as compared with the non-solvent, thereby causing a non-uniform distribution of the product on the treated surface.

The phosphoric monoesters of formula (I) are preparable by reacting the corresponding hydroxy-terminated polyperfluoroalkylene oxides $R_f-O-CFY-L-OH$ with $POCl_3$ in such molar ratios that $POCl_3$ is always in great excess. Generally, the $POCl_3$ /hydroxy-terminated product molar ratio ranges from 5:1 to 10:1, preferably from 6:1 to 8:1. The reaction is conducted by gradually dropping the hydroxy-terminated product into $POCl_3$, in the presence of a base, for example a tertiary amine, such as pyridin, triethylamine, tributylamine, at a temperature generally ranging from 50° to 100°C, preferably from 70° to 90°C. The reaction is conducted, always under stirring, until disappearance of the hydroxylic groups, what can be checked by infrared analysis. The $POCl_3$ excess is removed by distillation and the resulting product is hydrolized with water or with diluted hydrochloric acid. The organic phase is separated by extraction with a proper water-insoluble solvent for example a (chloro)fluorocarbon or methylchloroform. The separation is preferably carried out in the presence of a co-solvent, for example a water-soluble ketone, which has the function of preventing the formation of emulsions, which would hinder the separation of the organic product. From the organic phase, the product is separated according to conventional techniques, such as, for example, evaporation of the solvent.

From such reaction, the monoesters are obtained with high yields, usually in admixture with minor amounts of the corresponding di- and tri-esters.

The hydroxy-terminated polyperfluoroalkylene oxides $R_f-O-CFY-L-OH$ are known products and are preparable according to known methods starting from the corresponding polyperfluoroalkylene oxides having $-COF$ end groups. The starting polyperfluoroalkylene oxides containing end groups $-COF$ are described, for example, in patents: GB 1,104,482 (class (a)), US 3,715,378, US 3,242,218, US 3,242,218, EP 148,482, US 4,523,039, or also in patent application EP 340,740 and WO 90/03357.

In particular, products $R_f-O-CFY-L-OH$, where $L = -CH_2(OCH_2CH_2)_n-$ can be prepared by reduction of the corresponding fluorinated acids and, when $n \neq 0$, by subsequent ethoxylation reaction with ethylene oxide, conforming to what is described, for example, in patents: US 3,293,306, US 3,847,978, US 3,810,874 and US 4,814,372.

The products where $L = -CO-NR'-(CH_2)_q-$ are preparable by reacting the corresponding acyl fluorides with an

alkanolamine of formula $R'-NH-(CH_2)_q-OH$.

The monophosphoric acids utilized in the process of the present invention, besides imparting a particularly high oil- and water-repellency degree, are also capable of stably anchoring to the substrate, wherefore no migration phenomena to the substrate interior have been observed. Furthermore, the treated surface retains the oil- and water-repellency characteristics even after repeated washings with the most common cleaners.

The present invention will be now described more in detail by the following examples, which are given merely for purposes of illustration and are not intended to limit the scope of the invention.

The oil- and water-repellency degrees have been determined by observing the behaviour of an oil drop or water drop deposit onto the treated surface, taking two distinct parameters into consideration: drop sphericity and absorption time.

The drop sphericity is in itself a measure of the liquid repellency, and it can be determined by measuring the contact angle, i.e. the angle formed by the substrate plane and by the tangent to the drop surface in the point of contact with said plane. A perfectly spheric drop has a contact angle of 180° , while a flat drop has a contact angle tending to 0° .

Due to the irregularity of the "Tuscan cotto" surface, an accurate measurement of the contact angle is practically impossible, wherefore to discrete intervals of contact angle, a sphericity index according to the following scale has been correlated:

Sphericity index	Contact angle
A	about 180°
B	$150^\circ-180^\circ$
C	$120^\circ-150^\circ$
D	$90^\circ-120^\circ$
E	$< 90^\circ$

A perfectly spheric drop, which has a practically punctiform contact surface has a sphericity index A; nearly perfectly spheric drops, having an extremely reduced, but not punctiform surface contact surface, have been classified with B; index C has been attributed to drops exhibiting a good sphericity, having a rather wide contact surface, but always smaller than the dimensions of the drop. At D and E, the contact angle further decreases and, correspondingly the contact surface increases. The values reported in the examples represent an average calculated on 20 drops, having a volume of about $3 \mu\text{l}$ and deposited onto 25 cm^2 of "Tuscan cotto". For the water-repellency test, demineralized water has been utilized, while for the oil-repellency test, a paraffin oil having a viscosity of 20 cSt (commercial product: ESSO P60[®]) was utilized.

A correct evaluation of the liquid-repellency degree must take another parameter into account, namely the complete absorption time of the drop by the treated material surface (hereinafter referred to as t). Of course, in the case of water (water-repellency), the drop volume decreases in the time also due to the evaporation, wherefore there is a maximum time limit, within which the evaluation is still possible. At room temperature for a water drop of $3 \mu\text{l}$, a maximum limit of 30 minutes has been fixed. In the case of oil (oil-repellency), the evaporation is quite negligible, wherefore the maximum limit has been arbitrarily fixed at 7 days.

The begin of the absorption, if any, is indicated by the appearance of a dark halo at the drop base, which halo extends in the course of time and is accompanied by a proportional reduction of the drop volume.

The evaluation scale of the absorption index has been fixed as follows:

Absorption index	t	
	Water (min.)	Oil (hours)
a	0	0
b	2.5	1
c	5	2
d	10	3
e	15	4
f	20	5
g	25	6
h	30	24
i	--(*)	--(*)

(*) absence of absorption

Both for the water-repellency and for the oil-repellency, the dark halo appears within 5 minutes after the drop deposition at absorption indexes from (a) to (d), within 10 minutes at indexes from (e) to (h). No halo appears at absorption index (i).

In like manner as for the sphericity index, the values reported in the examples are the average calculated on 20 drops having a volume of about 3 μ l and deposited on 25 cm² of "Tuscan cotto".

On the basis of the sphericity index and absorption index determined according to the criteria described herein-above, the following evaluation scale has been fixed, which is valid for both the oil-repellency and the water-repellency:

Oil- or water-repellency	Sphericity index	Absorption index
0	E	a
1	E	b
2	E	c
3	E	d
4	E	e
5	E	f
6	E	g
7	D	h
8*	E	i
8	C	i
9	B	i
10	A	i

EXAMPLE 1

Onto a "Tuscan cotto" tiles measuring 5 x 5 cm it was dropped 1 ml of solution, at 1% by weight in isopropanol, of a mixture consisting for 90 mols-% of a phosphoric monoester corresponding to formula (I) with:

$L = -CH_2(OCH_2CH_2)-$; $m = 1$; $Z^+ = H^+$; R_1 is a chain of Galden[®] Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$,

EP 0 603 697 B1

$m/n = 20$. The remaining 10% consisted of a mixture of the corresponding diester ($m = 2$) and triester ($m = 3$).

The "cotto" was allowed to dry at room temperature for 2 hours. Then the water- and oil-repellency was evaluated conforming to the method described hereinbefore. The values are reported in table I.

5 The applied product was obtained as follows. 200 g (0.277 mols) of the corresponding hydroxy-terminated Galden® Y were gradually dropped (in 4 hours) into 225 g of POCl_3 ($\text{POCl}_3/\text{Galden}$ molar ratio = 6:1). The reaction was maintained under stirring for one hour more. During all the reaction time, the temperature was maintained at 90°C. The POCl_3 excess was then distilled off (at 50°C/20 mmHg). The distillation residue was then hydrolyzed by addition of 60 ml of H_2O . After addition of 90 ml of A113 ($\text{CF}_2\text{Cl}-\text{CFCI}_2$) and of 35 ml of acetone, the organic phase was separated in
10 an extraction funnel. The product contained in the organic phase was dried by evaporation of the solvents (at 80°C/1 mbar). There were obtained 192 g of a product consisting for 90 mols-% of monoester and for 10 mols-% of di- and triester, as it was checked by acidimetric titration and ^{31}P -NMR analysis.

EXAMPLES 2-3

15 Example 1 was repeated under the same conditions and with the same product utilizing solutions in isopropanol at 2.5% by weight (Ex. 2) and at 5.0% by weight (Ex. 3). The oil- and water-repellency values are reported in Table I.

EXAMPLES 4-6

20 Example 1 was repeated under the same conditions and with the same product, using as a solvent an isopropanol/water mixture in a 20:80 ratio by volume. Solutions at a concentration of 1.0% (Ex. 4), 2.5% (Ex. 5) and 5.0% (Ex. 6) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLES 7-8

25 Example 1 was repeated under the same conditions and with the same product, utilizing as a solvent an isopropanol/water mixture in a 50:50 ratio by volume. Solutions at a concentration of 2.5% (Ex. 7) and 5.0% (Ex. 8) by weight were applied. The water- and oil-repellency values are reported in table I.

EXAMPLES 9-10

30 Example 1 was repeated under the same conditions and with the same product, utilizing as a solvent a water/glycol/isopropanol mixture in a 69:17:14 ratio by volume. Solutions at a concentration of 2.5% (Ex. 9) and 5.0% (Ex. 10) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLES 11-12

40 Example 1 was repeated under the same conditions and with the same product, using as a solvent a water/glycol/isopropanol mixture in a 75:8:17 ratio by volume. Solutions at a concentration of 2.5% (Ex. 11) and 5.0% (Ex. 12) by weight were applied. The water- and oil-repellency values are reported in Table I.

EXAMPLE 13

45 Example 1 was repeated utilizing a solution, at 1% by weight in isopropanol, of a mixture composed for 90 mols-% of a phosphoric monoester corresponding to formula (I) where: $\text{L} = -\text{CH}_2(\text{OCH}_2\text{CH}_2)-$; $m = 1$; $\text{Z}^+ = \text{H}^+$; R_1 is a chain of Galden® Y (formula (II)), having $\text{Mn} = 900$, $\text{Mw/Mn} = 1.0$, $m/n = 20$. The remaining 10% was composed of the corresponding diester ($m = 2$) and triester ($m = 3$). The product was prepared according to the same method described in Example 1. The water- and oil-repellency values are reported in table II.

EXAMPLES 14-15

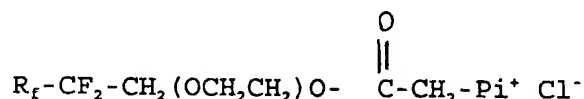
50 Example 1 was repeated utilizing solutions, at 0.5% (Ex. 14) and 1.0% (Ex. 15) by weight in isopropanol, of a mixture composed for 90 mols-% of a phosphoric monoester corresponding to formula (I) where: $\text{L} = -\text{CH}_2(\text{OCH}_2\text{CH}_2)-$; $m = 1$; $\text{Z}^+ = \text{H}^+$; R_1 is a chain of Galden® Y (formula (II)), having $\text{Mn} = 400$, $\text{Mw/Mn} = 1.0$, $m/n = 20$. The remaining 10% consisted of the corresponding diester ($m = 2$) and triester ($m = 3$). The product was prepared according to the same method described in Example 1. The water- and oil-repellency values are reported in Table II.

EXAMPLE 16

The phosphoric monoester of example 13 was salified with a hydroalcoholic KOH solution in a stoichiometric amount. After removal of the solvent by evaporation, the product was dissolved in A113 in such amount as to obtain a solution at 1% by weight. Such solution was applied on a "Tuscan cotto" according to the modalities described in Example 1. The water- and oil-repellency values are reported in table II.

EXAMPLE 17 (comparative)

Example 1 was repeated utilizing a solution, at 1% by weight in isopropanol, of a product of formula:



where Pi is a pyridinic ring, R_f is a chain of Galden[®] Y (formula (II)), with $M_n = 700$ and $M_w/M_n = 1.3$ and $m/n = 20$.

Such product was obtained - according to what is described in Italian patent application No. 360/MI92A, filed on February 20, 1992 by the Applicant - by esterification reaction of the hydroxy-derivative of formula:

$R_f - CF_2 - CH_2(OCH_2CH_2)OH$ with chloroacetic acid, and subsequent quaternization with pyridin in isopropanol.

The water- and oil-repellency values are reported in Table III.

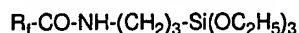
EXAMPLE 18 (comparative)

Example 1 was repeated utilizing a solution of 5% by weight in A113 of a mixture composed of $R_f - COO^- TEA^+$ (TEA = triethanolamine) and of the corresponding ketone $R_f - CO - CF_3$, in a 1:2 molar ratio, where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 2,700$, $M_w/M_n = 1.3$ and $m/n = 35$. Such mixture was obtained, according to conventional techniques, by acid hydrolysis and subsequent salification with TEA of the product deriving from the thermal treatment (200-250°C) of the rough product resulting from the photooxidation of hexafluoropropene with O_2 .

The water- and oil-repellency values are reported in Table III.

EXAMPLE 19 (comparative)

Example 1 was repeated using a solution at 1% by weight in isopropanol of a product of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$ and $m/n = 20$. Such product was obtained by reacting the corresponding acyl-derivative with 3-amino-propyl-triethoxysilane.

The water- and oil-repellency values are reported in table III.

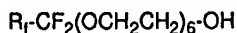
EXAMPLE 20 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a non-functionalized Galden[®] Y, corresponding to formula (II) with CF_3 end group, having $M_n = 1,500$, obtained via functional distillation of the corresponding commercial product.

The water- and oil-repellency values are reported in table III.

EXAMPLE 21 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$ and $m/n = 20$. Such product was obtained by reduction of the corresponding Galden[®] Y having -COF end groups and by subsequent ethoxylation with

ethylene oxide.

The water- and oil-repellency values are reported in table III.

EXAMPLE 22 (comparative)

5

Example 1 was repeated utilizing a solution at 4% by weight in A113 of a product of formula:



10 in admixture with a ketone of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 2,700$, $M_w/M_n = 1.3$ and $m/n = 35$. The acid/ketone molar ratio of about 1:2. It was the same product utilized in Example 18, but not subjected to salification with TEA.

15

The water- and oil-repellency values are reported in Table III.

EXAMPLE 23 (comparative)

20

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$ and $m/n = 20$. Such product was obtained by hydrolysis of the corresponding Galden[®] Y having -COF end groups.

25

The water- and oil-repellency values are reported in Table III.

EXAMPLE 24 (comparative)

30

Example 1 was repeated utilizing a solution at 1% by weight of A113 of a product of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 2,700$, $M_w/M_n = 1.3$ and $m/n = 35$, obtained from the product utilized in Example 22 by selective precipitation of the acids as calcium salts and by subsequent acidification.

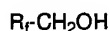
35

The water- and oil-repellency values are reported in Table III.

EXAMPLE 25 (comparative)

40

Example 1 was repeated utilizing a solution at 1% by weight in A113 of product of formula:



where R_f is a chain of Galden[®] Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$ and $m/n = 20$. Such product was obtained by reduction of the corresponding Galden^(R) Y having -COF end groups.

45

The water- and oil-repellency values are reported in Table III.

EXAMPLE 26 (comparative)

50

Example 1 was repeated utilizing a solution at 1% by weight in A113 of a product of formula:



where R_f is a chain of Galden^(R) Y (formula (II)), having $M_n = 700$, $M_w/M_n = 1.3$ and $m/n = 20$. Such product was obtained by reduction of the corresponding Galden^(R) Y having -COF end groups and by subsequent ethoxylation with ethylene oxide.

55

The water- and oil-repellency values are reported in Table III.

EXAMPLE 27 (comparative)

Example 1 was repeated utilizing a solution at 1% by weight in water of Surfion^(R) S-112 (salified perfluoroalkyl phosphate) produced by Asahi Glass Co..

The water- and oil-repellency values are reported in Table III.

TABLE I

EX.	SOLVENT	CONC. (% by wg.)	WATER-REPELLENCY	OIL-REPELLENCY
1	isopropanol	1.0	8	8
2	"	2.5	8	8
3	"	5.0	8	8
4	isoprop./H ₂ O	1.0	9	8
	20/80			
5	"	2.5	9	8
6	"	5.0	9	8
7	isoprop./H ₂ O 50/50	2.5	8	8
8	"	5.0	9	8
9	H ₂ O/glycol/isoprop. 69/17/14	2.5	8	8
10	"	5.0	8	8
11	H ₂ O/glycol/isoprop. 75/8/17	2.5	8	8
12	"	5.0	8	8

TABLE II

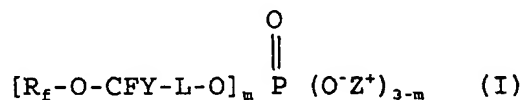
EX.	SOLVENT	CONC. (% by wg.)	WATER-REPELLENCY	OIL-REPELLENCY
13	isopropanol	1.0	9	8
14	"	0.5	8	8
15	"	1.0	8	8
16	A113	1.0	9	8

TABLE III

(Comparative Examples)			
EX.	PRODUCT	WATER-REPELLENCY	OIL-REPELLENCY
17	$R_fCF_2CH_2OCH_2CH_2O-CO-CH_2-Pi^+Cl^-$	0	7
18	$R_f-COO^-TEA^+ + R_f-CO-CF_3$	2	7
19	$R_f-CO-NH-(CH_2)_3-Si(OC_2H_5)_3$	0	3
20	R_f-CF_3	0	0
21	$R_f-CH_2(OCH_2CH_2)_6-OH$	0	7
22	$R_f-CO-OH + R_f-CO-CF_3$	0	3
23	R_f-COOH	0	6
24	R_f-COOH	0	8*
25	R_f-CH_2OH	0	6/7
26	$R_f-CH_2OCH_2CH_2-OH$	0	8*
27	$(C_nF_{2n+1})_m-P(O^+Z^-)_{3-m}$	2	8

Claims

1. A process for imparting oil- and water-repellency to the surface of a body of a porous ceramic material, which comprises applying onto said surface a phosphoric monoester of formula:



where:

L is a divalent organic group; $m = 1$; Y is -F or $-CF_3$; Z^+ is selected from: H^+ ; M^+ where M is an alkaline metal; $N(R)_4^+$ where groups R, like or different from one another, are H or C_1-C_6 alkyls; R_f is a polyperfluoroalkylene oxide chain.

2. The process of claim 1, wherein the phosphoric monoester of formula (I) is mixed with a phosphoric diester, corresponding to formula (I) where $m=2$, and/or a phosphoric triester, corresponding to formula (I) where $m=3$, in such amounts that the monoester content is at least equal to 80 mols-%.

3. The process of any of the preceding claims, wherein group L is selected from:

- (a) $-CH_2-(OCH_2CH_2)_n-$, where n is an integer ranging from 0 to 3;
- (b) $-CO-NR'(CH_2)_q-$, where R' is H or a C_1-C_4 alkyl; q is an integer ranging from 1 to 4.

4. The process of any of the preceding claims, wherein the R_f chains are composed of one or more repeating units, statistically distributed along the chain, selected from: (C_3F_6O) ; (C_2F_4O) ; $(CFXO)$, where X is -F or $-CF_3$; $(CYZ-CF_2CF_2O)$, where Y and Z, like or different from each other, are F, Cl or H, and have a number average molecular weight ranging from 350 to 3,000.

5. The process of claim 4, wherein the R_f chains have a number average molecular weight ranging from 400 to 1,000.

6. The process of claim 4 or 5, wherein the R_f chains are selected from the following classes:

(a)



where:

T is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X is $-F$ or $-CF_3$; Z is $-F$, $-Cl$ or $-CF_3$; m and n are numbers such that the n/m ratio ranges from 0.01 to 0.5 and the molecular weight is in the above-indicated range;

(b)

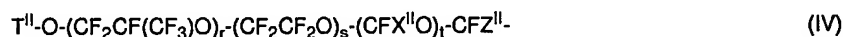


where:

 T^I is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-C_2F_4Cl$; Z^I is $-F$ or $-Cl$; p and q are numbers such that the q/p ratio ranges from 0.5 to 2 and the molecular weight is in the above indicated range;

(c)



where:

 T^{II} is a (per)fluoroalkyl group selected from:

$-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$; X^{II} is $-F$ or $-CF_3$; Z^{II} is $-F$, $-Cl$ or $-CF_3$; s and t are numbers such that r + s ranges from 1 to 50, the t/(r+s) ratio ranges from 0.01 to 0.05 and the molecular weight is in the above indicated range;

(d)



where:

 T^{III} is $-C_2F_5$ or $-C_3F_7$; u is a number such that the molecular weight is in the above indicated range;

(e)



where:

Y and Z, like or different from each other, are F, Cl or H; T^{IV} is $-CF_3$, $-C_2F_5$ or $-C_3F_7$; v is a number such that the molecular weight is in the above indicated range;

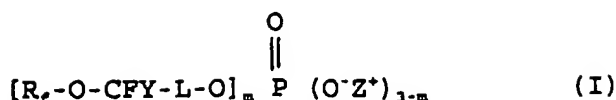
(f)



where:

 T^V is $-CF_3$ or $-C_2F_5$; w is a number such that the molecular weight is in the above indicated range.

7. The process of any of the preceding claims, wherein the phosphoric monoester is applied in the form of a solution at a concentration ranging from 0.1 to 5% by weight.
8. The process of claim 7, wherein the phosphoric monoester is applied in the form of a solution in a solvent selected from: aliphatic alcohols having 1 to 4 carbon atoms, fluorocarbons and chlorofluorocarbons optionally containing hydrogen, ketones and esters having 3 to 10 carbon atoms, methylchloroform, low molecular weight polyperfluoroalkylene oxides having fluoroalkyl end groups, or mixtures thereof.
9. The process of claim 7, wherein the phosphoric monoester is applied in the form of a solution in a solvent/non-solvent mixture selected from: ketone/water, alcohols/water, (chloro)fluorocarbons/dimethylformamide, methylchloroform/dimethylformamide.
10. Phosphoric monoesters having formula:

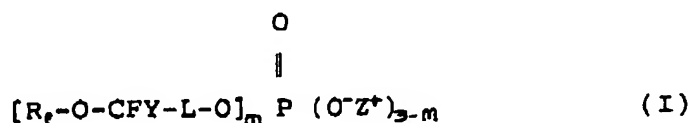


as defined in claims 1 to 6.

11. The process for preparing the phosphoric monoesters of claim 10, which comprises reacting, in the presence of a base, the corresponding hydroxy-terminated polyperfluoroalkylene oxides $R_f-O-CFY-L-OH$ with $POCl_3$, in such amount that the $POCl_3$ /hydroxy-terminated product molar ratio ranges from 5:1 to 10:1.

Patentansprüche

1. Verfahren, um der Oberfläche eines Körpers aus einem porösen Keramikmaterial öl- und wasserabweisende Eigenschaften zu verleihen, umfassend das Aufbringen eines Phosphorsäuremonoesters der nachfolgenden Formel:



wobei:

L eine bivalente organische Gruppe ist;

m = 1;

Y = -F oder -CF₃;

Z⁺ ausgewählt wird aus: H⁺; M⁺, wobei M ein Alkalimetall ist;

N(R)₄⁺, wobei die R-Gruppen, die gleich oder unterschiedlich sein können, H oder C₁-C₆-Alkyle sind;

R_f eine Polyperfluoralkylenoxidentkette ist.

2. Verfahren nach Anspruch 1, wobei der Phosphorsäuremonoester der Formel (I) mit einem Phosphorsäurediester vermischt wird, der der Formel (I) entspricht, wobei m=2, und/oder einem Phosphorsäuretriester, entsprechend der Formel (I), wobei m=3, in solchen Mengen, daß der Monoestergehalt wenigstens gleich 80 Mol-% beträgt.

3. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Gruppe L ausgewählt wird aus :

(a) -CH₂-(OCH₂CH₂)_n, wobei n ein Ganzzahliges im Bereich von 0 bis 3 ist;

(b) -CO-NR'-(CH₂)_q-, wobei R' H oder ein C₁ - C₄-Alkyl ist; q ein Ganzzahliges im Bereich von 1 bis 4 ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die R_f-Ketten aus einer oder mehreren sich wiederholenden Einheiten zusammengesetzt sind, die entlang der Kette statistisch verteilt vorliegen, ausgewählt aus: (C₃F₄O); (C₂F₄O); (CFXO), wobei X -F oder -CF₃ ist; (CYZ-CF₂CF₂O), wobei Y und Z, die gleich oder unterschiedlich sein können, F, Cl oder H sind,

und sie ein Molekulargewichts-Zahlenmittel von 350 bis 3000 aufweisen.

5. Verfahren nach Anspruch 4, wobei die R_f-Ketten ein Molekulargewichts-Zahlenmittel im Bereich von 400 bis 1000 aufweisen.

6. Verfahren nach Anspruch 4 oder 5, wobei die R_f-Ketten aus den nachfolgenden Klassen ausgewählt werden:

(a)



wobei:

T eine (Per)fluoralkylgruppe ist, ausgewählt aus:

-CF₃, -C₂F₅, -C₃F₇, -CF₂Cl, -C₂F₄Cl, -C₃F₆Cl; X ist -F oder -CF₃; Z ist -F, -Cl oder -CF₃; m und n Zahlen darstellen, so daß das Verhältnis n/m im Bereich von 0,01 bis 0,5 liegt und des Molekulargewicht im oben angegebenen Bereich liegt;

(b)

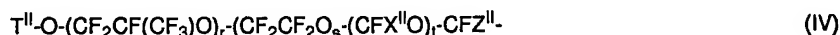


wobei:

T^I eine (Per)fluoralkylgruppe ist, ausgewählt aus:

-CF₃, -C₃F₅, -CF₂Cl, -C₂F₄Cl; Z^I ist -F oder -Cl, p und q Zahlen darstellen, so daß das Verhältnis q/p im Bereich von 0,5 bis 2 und das Molekulargewicht im oben angegebenen Bereich liegt;

(c)

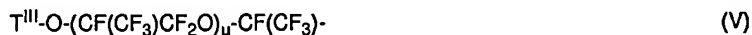


wobei:

T^{II} eine (Per)fluoralkylgruppe ist, ausgewählt aus:

-CF₃, -C₂F₅, -C₃F₇, -CF₂Cl, -C₂F₄Cl, -C₃F₆Cl; X^{II} ist -F oder -CF₃; Z^{II} ist -F, -Cl oder -CF₃; r, s und t Zahlen darstellen, so daß r + s im Bereich von 1 bis 50 liegt, das Verhältnis t/(r+s) im Bereich von 0,01 bis 0,05 und das Molekulargewicht im oben angegebenen Bereich liegt;

(d)



wobei:

T^{III} -C₂F₅ oder C₃F₇ ist;

u eine Zahl ist, so daß das Molekulargewicht im oben angegebenen Bereich liegt;

(e)



wobei:

Y und Z, die gleich oder unterschiedlich sein können, F, Cl oder H sind; T^{IV} -CF₃, -C₂F₅ oder -C₃F₇ ist; v eine Zahl ist, so daß das Molekulargewicht im oben angegebenen Bereich liegt;

(f)



wobei:

T^V -CF₃ oder -C₂F₅ ist; w eine Zahl ist, so daß das Molekulargewicht im oben angegebenen Bereich liegt.

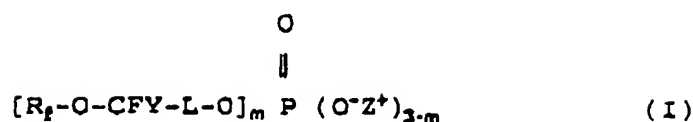
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Phosphorsäuremonoester in Form einer Lösung mit einer Konzentration im Bereich von 0,1 bis 5 Gew.-% aufgebracht wird.

8. Verfahren nach Anspruch 7, wobei der Phosphorsäuremonoester in Form einer Lösung in einem Lösungsmittel aufgebracht wird, ausgewählt aus: aliphatischen Alkoholen mit 1 bis 4 Kohlenstoffatomen, Fluorkohlenstoffen und Chlorkohlenstoffen, die wahlweise Wasserstoff enthalten, Ketonen und Estern mit 3 bis 10 Kohlenstoffatomen, Methylchloroform, Polyperfluoralkylenoxiden mit einem niedrigen Molekulargewicht mit Fluoralkylendgruppen, oder Mischungen hiervon.

9. Verfahren nach Anspruch 7, wobei der Phosphorsäuremonoester in Form einer Lösung in einer Lösungsmittel/Nichtlösungsmittel-Mischung aufgebracht wird, ausgewählt aus:

Keton/Wasser, Alkoholen/Wasser; (Chlor)fluorkohlenstoffen/Dimethylformamid, Methylchloroform/Dimethylformamid.

10. Phosphorsäuremonoester der Formel:

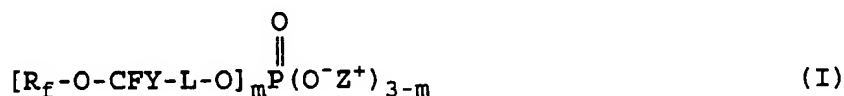


definiert in den Ansprüchen 1 bis 6.

11. Verfahren zur Herstellung der Phosphorsäuremonoester nach Anspruch 10, umfassend das Umsetzen, in Gegenwart einer Base, der entsprechenden hydroxyl-terminierten Polyperfluoralkylenoxide $\text{R}_f\text{-O-CFY-L-OH}$ mit POCl_3 , in einer solchen Menge, daß das POCl_3 /hydroxyl-terminierte Produkt-Molverhältnis im Bereich von 5:1 bis 10:1 liegt.

Revendications

1. Procédé pour conférer un caractère oléorésistant et hydrophobe à la surface d'un corps d'une matière céramique poreuse, lequel procédé comprend l'application sur ladite surface d'un monoester phosphorique de formule :



dans laquelle :

- L est un groupe organise divalent ;
 - $m = 1$;
 - Y représente -F ou $-\text{CF}_3$;
 - Z^+ est choisi parmi H^+ ; M^+ où M est un métal alcalin ; N(R)_4^+ où les groupes R, identiques ou différents les uns des autres, représentent H ou alkyle en $\text{C}_1\text{-C}_6$;
 - R_f est une chaîne de poly(perfluoroalkylène oxyde).
2. Procédé selon la revendication 1, dans lequel le monoester phosphorique de formule (I) est mélangé avec un diester phosphorique, correspondant à la formule (I) où $m = 2$, et/ou un triester phosphorique, correspondant à la formule (I) où $m = 3$, dans des quantités telles que la teneur en monoester soit au moins égale à 80% en moles.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le groupe L est choisi parmi :
- (a) $-\text{CH}_2\text{-(OCH}_2\text{CH}_2)_n-$,
où n est un entier se situant dans la plage de 0 à 3 ;
 - (b) $-\text{CO-NR}'\text{-(CH}_2)_q-$,
où :
 - R' représente H ou un alkyle en $\text{C}_1\text{-C}_4$;
 - q est un entier se situant dans la plage allant de 1 à 4.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel les chaînes R_f sont composées d'un ou plusieurs motifs répétitifs, distribués de façon statistique le long de la chaîne, choisis parmi : $(\text{C}_3\text{F}_6\text{O})$; $(\text{C}_2\text{F}_4\text{O})$, (CFXO) , où X représente -F ou $-\text{CF}_3$; $(\text{CYZ-CF}_2\text{CF}_2\text{O})$, où Y et Z, identiques ou différents les uns des autres, représentent F, Cl ou H, et ont une masse moléculaire moyenne en nombre se situant dans la plage allant de 350 à 3 000.
5. Procédé selon la revendication 4, dans lequel les chaînes R_f ont une masse moléculaire moyenn en nombre se situant dans la plage allant de 400 à 1000.

6. Procédé selon l'une des revendications 4 ou 5, dans lequel les chaînes R_i sont choisies parmi les classes suivantes :

(a)



ou :

- T est un groupe (per)fluoroalkyle choisi parmi : $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$;
- X représente -F ou $-CF_3$;
- Z représente -F, -Cl ou $-CF_3$;
- m et n sont des nombres tels que le rapport n/m se situe dans la plage allant de 0,01 à 0,5 et la masse moléculaire se trouve dans la plage indiquée ci-dessus ;

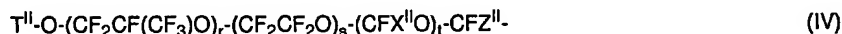
(b)



où :

- T^I est un groupe (per)fluoroalkyle choisi parmi $-CF_3$, $-C_2F_5$, $-CF_2Cl$, $-C_2F_4Cl$;
- Z^I représente -F ou -Cl ;
- p et q sont des nombres tels que le rapport q/p se situe dans la plage allant de 0,5 à 2 et la masse moléculaire se situe dans la plage indiquée ci-dessus ;

(c)



où :

- T^{II} est un groupe (per)fluoroalkyle choisi parmi : $-CF_3$, $-C_2F_5$, $-C_3F_7$, $-CF_2Cl$, $-C_2F_4Cl$, $-C_3F_6Cl$;
- X^{II} représente -F ou $-CF_3$;
- Z^{II} représente -F, -Cl ou $-CF_3$;
- r, s et t sont des nombres tels que $r + s$ se situe dans la plage allant de 1 à 50, le rapport $t/(r+s)$ se situe dans la plage allant de 0,01 à 0,05 et la masse moléculaire se situe dans la plage indiquée ci-dessus ;

(d)



où :

- T^{III} représente $-C_2F_5$ ou $-C_3F_7$;
- u est un nombre tel que la masse moléculaire se situe dans la plage indiquée ci-dessus ;

(e)



où :

- Y et Z, identiques ou différents l'un de l'autre, représentent F, Cl ou H ;
- T^{IV} représente $-CF_3$, $-C_2F_5$ ou $-C_3F_7$;
- v est un nombre tel que la masse moléculaire se situe dans la plage indiquée ci-dessus ;

(f)

